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TRIFLUOROACETOXY-PHENYLSELENATION OF NITROOLEFINS REGIOSELECTIVE PREPARATION OF NITROALLYLIC ALCOHOL DERIVATIVES AND THEIR USE AS MULTIPLE COUPLING REAGENTS

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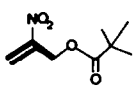
Abstract - *It has been shown in previous papers that the pivalate of 2-nitro-2-propen-1-ol (NPP,* 1*), a nitroolefin with allylic leaving group, can be used as a versatile multiple coupling reagent. The present contribution describes the preparation of NPP analogues, substituted in the 1- and/or 3-position of the allylic carbon skeleton. Standard methods of nitroaliphatic chemistry readily provide symmetrically substituted derivatives such as the cyclohexenes* (7) *and the indenes* (8)*, while unsymmetrical ones such as the phenyl NPP* 9 *are not so easy to prepare. This situation is now greatly improved by a regioselective method of introducing an allylic pivaloyloxy group into nitroolefins: in the first step of the four-step sequence a phenylseleno- and a trifluoroacetoxy-group are added across the nitroolefinic double bond* (10 → 11)*, then, the trifluoroacetate is cleaved, and the resulting nitro-phenylseleno-alcohol* 12 *is oxidized with elimination to the nitroallylic alcohols* 13*. These are pivalated by pivalic anhydride/* BF_3*·etherate* (→ 14)*. - The regioselective preparation of the products* 16-34 *of nitroallylation of various nucleophiles with substituted NPP-type reagents demonstrates the broad scope of these multiple coupling reagents. Due to the multitude of conversions of the nitro group, these reagents provide access to a great variety of structures without* NO_2*-substituents, cf.* 2 *and* 3*. The mechanism of the reaction of NPP-derivatives is discussed.*

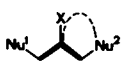
A) INTRODUCTION

Several years ago[3], we have shown that the pivaloyloxy substituted 2-nitropropene 1 can be used for coupling with two different nucleophilic components[4], see 2. This yields nitroalkanes 2, X=H/NO_2, which in turn can be subjected to the transformations typical of the nitro group[5]. Thus, reduction furnishes amines, substitution of NO_2 by OH and by H is possible, the nitrogroup can act as leaving group in eliminations, the *Nef* reaction transforms the resulting secondary nitroalkanes to ketones, oximes can be produced, nitroolefins are excellent dienophiles in *Diels-Alder* reactions, and secondary nitroalkanes are highly reactive as donor components of *Michael* additions to α,β-unsaturated carbonyl compounds. Thus, all the structures indicated by the *formulae* 2 and 3 can be built up using NPP (1) as a coupling reagent. A full paper with numerous examples has appeared[4].

We found, that NPP is much more reactive than a simple 2-nitro-1-alkene. Therefore, the first coupling step cleanly produces products of nitroallylation of the nucleophiles (Nu^1) employed. Also, the pivaloyloxy group has a sterically protected[6] carbonyl center which does not compete with the nitroolefinic acceptor double bond. Therefore, even the most reactive nucleophiles such as alkyl- and arylli-

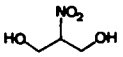


1
(NPP)



2
X=H/NO_2, H/NH_2
H/R, O, NR,
H/OH, R/OH

3



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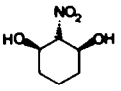

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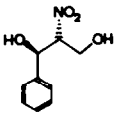
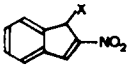
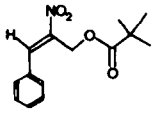


6(ℓ)

7
a: X=OH
b: X=OCO^{t}Bu
c: X=Cl



8
a: X=OH
b: X=OCO^{t}Bu
c: X=Cl



9

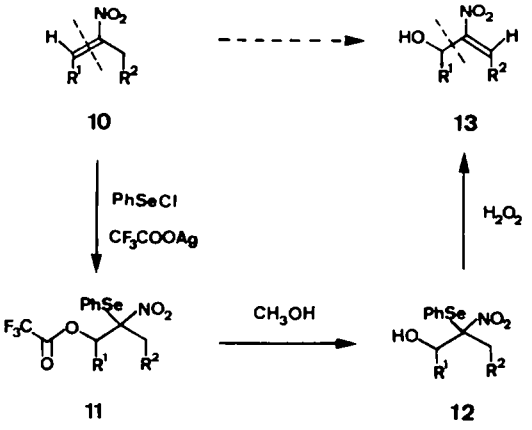
thium compounds can be added to NPP. The very special reactivity of this system made it desirable to develop synthetic routes also to substituted NPP-derivatives, which was the goal of our recent studies in this area.

B) NPP-Derivatives from 2-Nitro-1.3-diols

The parent compound, NPP itself, is prepared from nitromethane and formaldehyde through the nitropropane-diol 4. Thus, other symmetrically substituted derivatives should also be accessible from nitromethane and other aldehydes. We prepared the cyclohexene analogues 7b and 7c of NPP from the known nitrodiol 5 which is readily made as a single trans,trans-diastereomer from nitromethane and glutaric dialdehyde[7]. Dehydration of 5 with DCC[8] gives the nitroallylic alcohol 7a which is converted to those NPP-analogues. Similarly, the suitably substituted indenes 8 are prepared from nitromethane and phthalic dialdehyde. Unsymmetrically substituted 2-nitro-1.3-propane-diols are less readily available. They result from nitroaldol additions of nitromethane to two different aldehydes[9]. A product (6) of this type, made from nitromethane, formaldehyde, and benzaldehyde, is the intermediate of an industrial process for the synthesis of the antibiotic chloroamphemicol[10]. Esterification of both OH-groups of 6 to a di-pivalate and elimination gives the phenyl-NPP 9 of E-configuration.

C) Allylic Hydroxylation of Nitroolefins with Double-bond Shift, Using a Selenium Reagent

Being electrophiles themselves, nitroolefins are normally not subject to attack by other electrophiles. In contrast, they are typical *Michael* acceptors for nucleophiles[5,11,12]. Only the most reactive electrophiles such as bromine[11] and mercury(II)acetate[2] have been added to nitroolefins. Since we wanted to prepare pivalates of nitro-allylic alcohols, we first tried to add the phenylseleno-group[13] and a pivaloyloxy-group across nitro-olefinic double bonds. Even with silver pivalate, the reaction

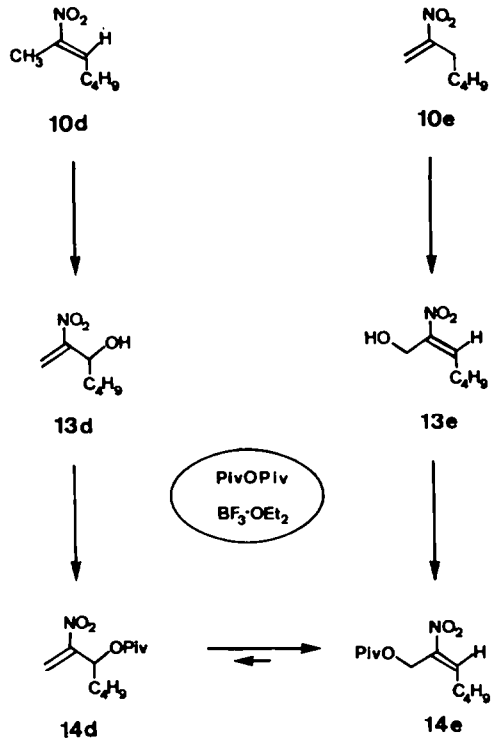


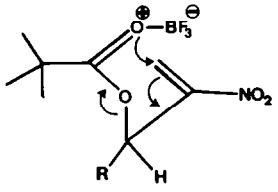
10-13	a	b	c	d	e	f	g
R^1	H	CH_3	C_2H_5	C_4H_9	H	C_5H_{11}	$(CH_2)_3$
R^2	H	H	H	H	C_4H_9	H	

(7a is obtained from 12g)

did not proceed. We therefore first added phenylselenyl chloride/silver trifluoroacetate[14-16] to nitroolefins 10. The resulting trifluoroacetates 11 were solvolyzed to give α-phenylselenyl-β-hydroxy-nitroalkanes 12. These in turn were treated with hydrogen peroxide to induce the elimination of the phenylselenyl group[17-19].

As usually this elimination occurred regioselectively, away from the hydroxylated carbon atom[18], to give the allylic alcohols 13. The intermediate seleno-compounds 12 can be isolated, purified, and characterized. In contrast to the analoguous addition to acrylate[15], the present reaction is totally regioselective (by ^{1}H-NMR analysis). Both, 11 and 12, are single diastereomers if configurationally pure nitroolefins 10 are employed. We assume that the normal *"trans"*-addition to the double bond takes place[19]. It is also possible to do the three steps leading from the nitroolefins 10 to the allylic alcohols 13 without purification of intermediates. The overall yields are between 50 and 70 %, and the R^1/R^2-groups with which the process was carried out are specified underneath the *formulae* in the accompanying flow sheet. The olefin 13e with $R^2 \neq H$, is isolated as pure E-isomer[20]. Since the starting materials, the nitroolefins 10, are prepared from aldehydes R^1CHO and nitroalkanes $R^2CH_2CH_2NO_2$ by nitroaldol condensation[8,21] as indicated by the dotted line in the *formula*, the hydroxylation with double bond shift provides products 11 which are formally derived from aldehydes and nitrovinyl-d^1-reagents, hitherto not available as such[1,22].





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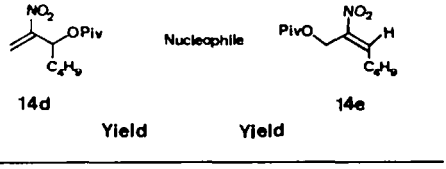
D) BF_3·Etherate Induced Pivaloylation of Nitroallylic Alcohols 13 Under Conditions of Kinetic or Thermodynamic Control

Due to the high reactivity of NPP-type nitroolefins, the pivaloylation of alcohols 13 is not possible under the standard conditions, using an acylating reagent and a base. Since nitroolefins are generally much more stable in the presence of acid, we employed pivalic anhydride and boron trifluoride etherate[23] for converting the alcohols 13 to esters 14. If this reaction, which is performed in the anhydride as a solvent, is carried out at room temperature, the two isomeric allylic alcohols 13d and 13e were esterified selectively to the pivalates 14d (70 %) and 14e (70 %), respectively. We noticed, however, that the ester 14d of the secondary alcohol rearranged slowly to the ester 14e of the primary alcohol on prolonged treatment under the reaction conditions. At 80°C the secondary alcohol was converted directly to the ester of the primary alcohol (67 %). The observed 1.3-shift of the oxygen function may be taking place through a concerted [3.3]-sigmatropic shift following the scheme of the *Claisen-Cope* rearrangement, see 15, with formation of the thermodynamically more stable product[24] which has a terminal OPiv-group and E-configuration. Thus, the more highly substituted nitroolefin 10d can be used as a starting material for both NPP-type products 14d and 14e, with terminal and internal double bond, respectively. Nitroolefins of type 10d with trisubstituted double bonds are prepared regioselectively from nitroalkanes and aldehydes under certain conditions. In a convenient procedure, the dehydration of the intermediate nitroaldols is achieved with dicyclo-

hexyl-carbodiimide under Cu(I)-catalysis[8].

E) Additions of Nucleophiles to the Isomeric Nitro-heptenyl-pivalates 14d and 14e

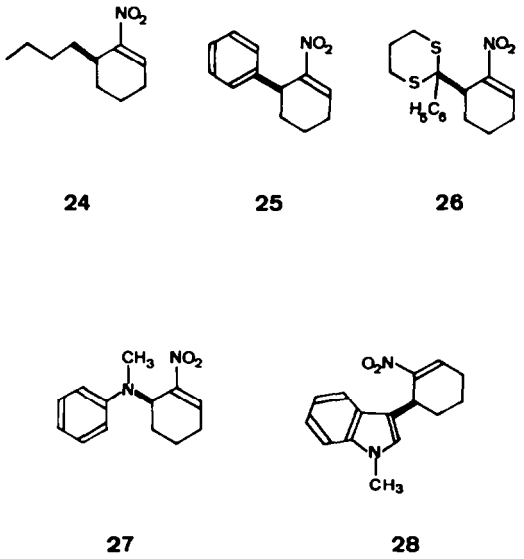
In order to prove the viability of the concept of using isomeric NPP-derivatives as selective coupling reagents[4], we have added a number of nucleophiles to the nitroolefins 14d and 14e. In each case, the two nitroolefins were allowed to react with the nucleophile under identical conditions. Very similar yields of the isomeric products of nitroallylation were obtained with the more reactive nucleophiles such as butyllithium (→ 16, 17) and the lithium enolates of cyclopentanone (→ 18, 19) and of cyclohexanone (→ 20, 21). The higher reactivity of the NPP-derivative 14d with terminal double bond as compared with the isomer 14e with trisubstituted double bond, coupled with a lower reactivity of the product from the former reagent is responsible for the good yield of 22 obtained from 14d and N-methyl-indole, as compared with the poor yield of 23 from 14e and the same nucelophile. - The products 16, 18, 20, 22 with trisubstituted double bonds are isolated as single diastereomers with E-configuration of the double bond[20].

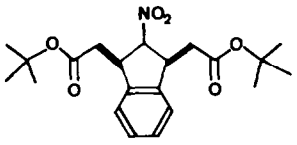


F) Nitroallylations with the Reagents 7, 8, and 9[25]

The 2-nitro-2-cyclohexen-1-yl pivalate 7b reacts in good (63 %) to excellent (92 %) yields with various nucleophiles. Obviously, it is a much more reactive electrophile than the parent nitrocyclohexene itself[26]. Products were isolated after addition of butyllithium (→ 24), phenyllithium (→ 25), 2-lithio-2-phenyl-1,3-dithiane (→ 26), and N-methyl-aniline (→ 27). In contrast to NPP (1), 7b does however not react with N-methylindole even at 80°C; only with the more reactive 1-chloro-2-nitro-2-cyclohexene (7c), the reaction takes place to give the adduct 28 in 47 % yield.

The indene derivative 8 was the only relative of NPP to which a stepwise addition of two different nucleophiles did not appear to be feasible: only the adduct 29 of two t-butyl acetate enolates could be isolated! Phenyl-NPP (9) reacts with enolates to give exclusively products (30, 31) of phenyl-nitro-allylation. Also,





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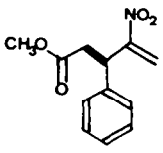

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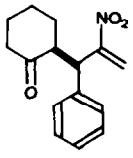
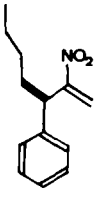


31 (75% ds)



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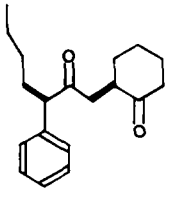
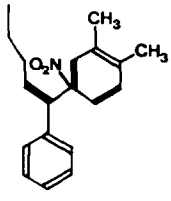


33 (75% ds)

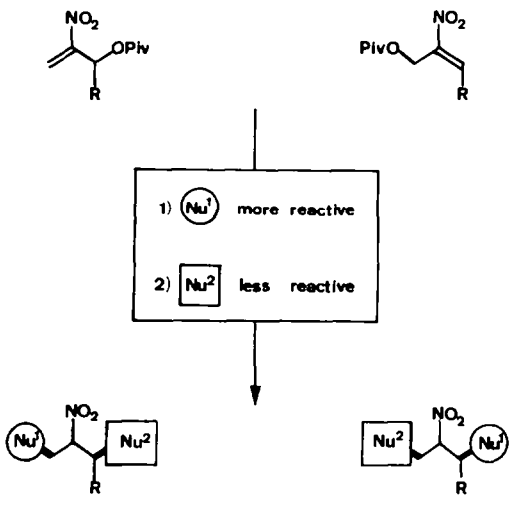


34 (60% ds)

when combined with butyllithium, 9 gave a 92 % yield of the 3-phenyl-2-nitro-1-heptene (32), to which the silyl enol ether of cyclohexanone was added as a second nucleophile, with an *in-situ Nef* reaction[27] (→ 33). Finally, the product 34 of a *Diels-Alder* reaction was isolated in 89 % yield after reaction of 32 with 2.3-dimethyl-1.3-butadiene.

G) DISCUSSION AND CONCLUSIONS

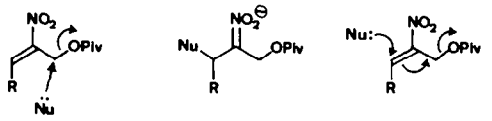
It is demonstrated, that the useful properties of 2-nitro-2-propen-1-yl (2.2-dimethyl)propionate (NPP, 1) as coupling reagent for highly convergent syntheses are also present in derivatives with conjugative (8, 9) and non-conjugative (7, 14) substituents, see the products 16-34. The oxo-selenation of nitroolefins is introduced as an effective means of preparing nitroallylic alcohols (13) from simple nitroolefins (10). This key reaction allows an overall regioselective allylic pivaloyloxylation of nitroolefins. The access to either constitutional isomer by the selenium-based process is an important improvement for the application of NPP-type multiple coupling reagents: As we have shown previously[4], the sequence of addition of different nucleophiles can not be arbitrarily chosen; it is advantageous, and sometimes only possible to add the more reactive nucleophile first; thus, the two isomeric products are not equally well prepared from the same substituted nitroallylating reagent by just interchanging the sequence of addition of Nu^1 and Nu^2. As is outlined in the accompanying scheme, the two constitutional isomers 35 and 36 can now be prepared from the two isomeric NPP-derivatives, using the same sequence of addition of Nu^1 and Nu^2.



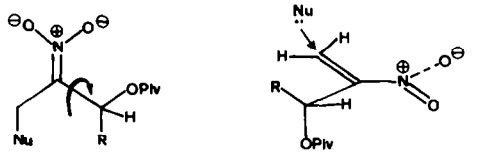
35 36

The reactions of NPP derivatives with trisubstituted double bonds, such as 9 and 14e, prove unambiguously that the nitroallylations do not occur by direct S_N2-substitution, see 37. Our growing experience with these reagents makes us believe that with the most reactive nucleophiles such as organolithium compounds and lithium enolates the "stop and go" mechanism, see 38, is followed, while we cannot exclude the S_N2'-route (39) with the less reac-

tive nucleophiles such as enanimes, anilines or indoles.



37 38 39



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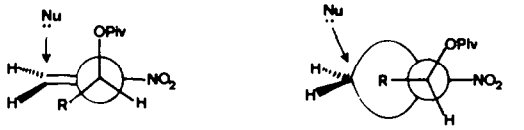

42 43

The formation of the thermodynamically more stable products with E-configuration from the NPP-derivatives with terminal double bond is also compatible with both mechanisms, see 40-43. The intermediate nitronate 40 with free rotation around the single bond would be expected to eliminate the pivalate group to give the more stable product. But also in the transition states of S_N2'-substitutions with anti-periplanar (41)[4], with syn-periplanar (42)[28] or with staggered (43)[29] pivaloyloxy group, the repulsion between the nitro- and the R-group is expected to favor the formation of the E-product.

H) EXPERIMENTAL

General remarks. Melting points and boiling points are uncorrected. M.p. were determined on a Büchi 510 m.p. apparatus. B.p. are air-bath-temperatures during Kugelrohr distillations in a *Büchi* GKR-50 apparatus. Spectra were recorded with the following instruments: IR: *Perkin-Elmer*-spectrometer 297; ^{1}H-NMR: *Varian*-EM-390 (90 MHz), *Varian*-XL-100 (100 MHz) and *Brüker* (300 MHz); ^{13}C-NMR: *Varian*-CFT-20 (20 MHz); MS: *Hitachi Perkin-Elmer*-RMU-6M. IR data are presented in cm^{-1}. NMR spectra were recorded with $(CH_3)_4Si$ as internal standard. The diastereomeric composition (^{30}) of crude products was determined by ^{1}H-, ^{13}C-NMR and/or by capillary GC, using a 13.5 m SE-54 or a 19 m Pluronic L64 column. All reactions involving Li derivatives were carried out under anhydrous conditions in an argon atmosphere. Flash chromatography was performed according to the method described by *W.C. Still* et al.[31]. Nitroolefins 10 were prepared from aldehydes and nitroalkanes by fluoride catalized nitroaldol condensation[21] and subsequent dehydration with dicyclohexyl-carbodiimide under Cu(I)-catalysis[8].

2-Nitro-2-cyclohexen-1-ol (7a). A mixture of 30 g (189 mmol) nitrodiol 5[7], 42.3 g (205 mmol) dicyclohexenyl-carbodiimide and 620 mg Cu-(1)-Cl in 130 ml dioxan was stirred in the dark at room temp. during 24 h. The mixture was diluted with 150 ml CCl_4 and cooled to 0°C. The precipitate was filtered off and the solvent removed on vacuo. Flash chromatography (CCl_4/MeOH 9:1) (ca. 5 g crude product pro chromatography) gave 16.2 g (61 %) 7a as a pale brown oil. IR (CCl_4): 3600 m, 3520 m, 2960 m, 1740 w, 1665 w, 1520 s. ^{1}H-NMR ($CDCl_3$): δ 7.31 (t, J = 3 Hz, 1 H); 4.75 (bt, 1 H); 3.40 (bs, 1 H); 2.82 (m, 2 H); 1.60-2.10 (m, 4 H).

2'-Nitro-2'-cyclohexen-1'-yl 2,2-dimethylpropanoate (7b). A mixture of 7.6 g (53.1 mmol) 2-Nitro-2-cyclohexen-1-ol (7a), 40 ml pivalic anhydride, 1 ml $BF_3 \cdot OEt_2$ was heated at 100°C during 0.75 h. The anhydride was evaporated at 60°C and 0.1 mm Hg and the residue purified by flash chromatography ($AcOEt/CH_2Cl_2$ 1.5:8.5). Distillation (80°C/10^{-5} mm Hg) gave 9.1 g (94 %) 7b as a yellow oil, which slowly crystallised at -20°C. M.p. 22°C. IR (CCl_4): 2980 m, 2940 m, 1730 s, 1670 w, 1520 s. ^{1}H-NMR ($CDCl_3$): δ 7.51 (t, J = 3 Hz, 1 H); 5.87 (bt, 1 H); 2.5 (m, 2 H); 1.7-2.2 (m, 4 H); 1.18 (s, 9 H). MS *m/e*: 181, 126, 125, 77, 41. (Found: C, 58.23; H, 7.45; N, 6.32. Calc for $C_{11}H_{17}NO_4$: C, 58.14; H, 7.54; N, 6.16.)

6-Chloro-1-nitrocyclohexene (7c). A solution of 3.8 g (265 mmol) 7a and 25 g (246 mmol) SO_2Cl in 50 ml of benzene was refluxed for 0.75 h. The solvent was removed on vacuo and the residue purified by flash chromatography (CH_2Cl_2/AcOEt 9:1). Yield: 3.53 g 7c (82 %). An analytical sample was obtained by distillation. B.p. 50°C/10^{-5} mm Hg. IR (CCl_4): 2960 m, 2880 m, 1670 m, 1530 s. ^{1}H-NMR (CCl_4): δ 7.36 (m, 1 H); 5.21 (bs, 1 H); 1.8-2.6 (m, 6 H). MS *m/e*: 163, 161, 125, 79, 41, 36. (Found: C, 44.51; H, 4.87; N, 8.48. Calc for $C_6H_8NO_2Cl$: C, 44.60; H, 4.99; N, 8.67.)

2-Nitro-3-pivaloyloxyindene (8b). A mixture of 2 g (11.3 mmol) 8a[32,33], 10 ml pivalic anhydride and 0.3 ml $BF_3 \cdot OEt_2$ was heated at 80°C during 1 h. The anhydride was evaporated at HV during 30 h. The solid residue was dissolved in 50 ml pentan, charcoal was added and the mixture was refluxed for 5 min. The solution was filtered and concentrated at reduced pressure.

This gave 1.65 g (56 %) yellow crystals. An analytical sample was obtained by recrystallisation from pentane. M.p. 82-83°C. IR ($CHCl_3$): 3030 m, 2980 s, 1735 s, 1615 m, 1605 m, 1580 s, 1510 s. ^{1}H-NMR ($CDCl_3$): δ 7.86 (s, 1 H); 7.55-7.35 (m, 4 H); 6.78 (s, 1 H); 1.22 (s, 9 H). MS *m/e*: 261, 215, 187, 57, 41. (Found: C, 64.52; H, 5.77; N, 5.32. Calc for $C_{14}H_{15}NO_4$: C, 64.36; H, 5.79; N, 5.36.)

2-Nitro-3-chlorindene (8c). A solution of 4.8 g (27.1 mmol) 8a and 25 g (245.8 mmol) SO_2Cl in 50 ml of benzene was refluxed during 2 h. The solution was concentrated at reduced pressure and the residue crystallised from benzene/pentane. Recrystallisation from ether/pentane (charcoal) gave 2.6 g (40 %) 8c as green-yellow crystals. M.p. 94-95°C. IR ($CHCl_3$): 3080 w, 1612 m, 1605 m, 1575 s, 1515 s, 1465 m. ^{1}H-NMR ($CDCl_3$): δ 7.86 (s, 1 H); 7.70-7.30 (m, 4 H); 5.64 (s, 1 H). MS *m/e*: 197, 195, 149, 114, 36. (Found: C, 55.11; H, 3.12; N, 7.09; Cl, 18.20. Calc for $C_9H_6NO_2Cl$: C, 55.26; H, 3.09; N, 7.16; Cl, 18.13.)

2'-Nitro-3'-phenyl-3'-pivaloyloxy-1'-propyl 2,2-dimethylpropanoate. A suspension of 200 g (1.014 mol) 6(ℓ) in 400 ml of CH_2Cl_2 was refluxed and 366 g (3.042 mol) of pivalic chloride were slowly added with vigourous stirring. The HCl-evolution was monitored by a bubbler. After 7 h no more HCl was formed and the mixture was cooled and allowed to stand for 12 h at room temp. The solvent and excess pivalic chloride were removed by evaporation. The solid residue was dissolved in 1.5 l CH_2Cl_2, washed successively with 0.2 M NaOH-solution (3x100 ml) and water until the acqueous layer was neutral. The crude product (358 g/97 %) was isolated as yellow crystals. M.p. 69°C. IR ($CHCl_3$): 3040 m, 2970 m, 1730 s, 1560 s. ^{1}H-NMR ($CDCl_3$): δ 6.15 (d, J = 10 Hz, 1 H); 5.18 (m, 1 H); 4.19 (d, J = 6 Hz); 1.13 (s, 18 H).

E-2'-Nitro-3'-phenyl-2'-propen-1'-yl 2,2-dimethylpropanoate (9). A mixture of 12 g (32.9 mmol) of 2'-nitro-3'-phenyl-3'-pivaloyloxy-1'-propyl 2,2-dimethylpropanoate and 4.03 g (49.21 mmol) of sodium acetate in 86 ml of ether were vigorously stirred at room temp. for 18 h. The sodium acetate was filtered off and the filtrate was washed (1) with $NaHCO_3$-solution and (2) with water and dried over $MgSO_4$. The solvent was removed under reduced pressure. Recrystallisation from Et_2O/pentane gave 8.64 g (95 %) 9 as yellow crystals. M.p. 69°C. ^{1}H-NMR ($CDCl_3$): δ 8.35 (s, 1 H); 7.50 (s, 5 H); 5.20 (s, 2 H); 1.21 (s, 9 H). MS *m/e*: 262, 218, 217, 57, 41, 18. (Found: C, 63.72; H, 6.54; N, 5.36. Calc for $C_{14}H_{17}NO_4$: C, 63.87; H, 6.51; N, 5.32.)

Addition of benzeneselenyl trifluoroacetate to nitroolefins

General prodecure. A 10 mmol run is described. To a suspension of 10 mmol silvertrifluoroacetate in 20 ml of CH_2Cl_2 under argon was added a solution of 10 mmol benzeneselenyl chloride in 5 ml of CH_2Cl_2. A precipitate of silver chloride and a yellow/orange solution resulted. To this mixture was added 10 mmol of the nitroolefin. After 3-24 h stirring by room temp., the heterogenous solution was filtered through celite and the solvent removed in vacuo. The resulting compound was pure by ^{1}H-NMR. The β-trifluoroacetoxy nitroselenides could be purified neither by chromatography nor by distillation and were directly hydrolysed to the corresponding β-hydroxy nitroselenides.

2-Nitro-2-phenylselenopropyl-trifluoroacetate (11a). From 0.435 g (5 mmol) of 2-nitropropene, 1.105 g (5 mmol) of silvertrifluoroacetate and 0.935 g of benzeneselenyl chloride 1.73 g (97 %) of 11a was obtained as a yellow-orange oil. IR (Film): 1795 s, 1495 s, 1470 w, 1225 s, 1150 s. ^{1}H-NMR ($CDCl_3$): δ 7.70-7.40 (m, 5 H); 4.95-4.60 (AB syst., J_{AB} = 12 Hz, 2 H); 1.94 (s, 3 H); MS *m/e*: 357, 311, 309, 157, 43.

1-Methyl-2-Nitro-2-phenylseleno-propyl-trifluoroacetate (11b). From 2-nitro-2-butene (0.850 g/8.4 mmol) (mixture of *cis/trans* isomers ca. 1.5:1), 1.620 g (8.4 mmol) of benzeneselenyl chloride, 1.850 g (8.4 mmol) of silvertrifluoroacetate 2.982 g (8.05 mmol/96 %) of 11b was obtained as yellow oil. Two diastereomers were obtained in ratio ca. 1.4:1. IR (Film): 3060 w, 3000 w, 1795 s, 1550 s, 1230 s, 1160 s. ^{1}H-NMR ($CDCl_3$): δ 7.61-7.35 (m, 5 H); 5.71 and 5.63 (q, J = 2 Hz, 1 H); 1.88 and 1.78 (s, 3 H); 1.66 and 1.41 (d, J = 2 Hz, 3 H); MS *m/e*: 371, 324, 156, 154, 43.

1-Ethyl-2-nitro-2-phenylseleno-propyl-trifluoroacetate (11c). Treatment of 7 g (60.8 mmol) of 2-nitro-2-pentene with 61 mmol of $PhSeO_2CCF_3$ (prepared as usual) gave 22.65 g (97 %) of 11c as an orange oil. IR (Film): 2980 m, 1795 s, 1545 s, 1440 s, 1220 s, 1150 s. ^{1}H-NMR ($CDCl_3$): δ 7.70-7.30 (m, 5 H); 5.80-5.60 (m, 1 H); 1.86 and 1.75 (s, 3 H); 1.80-1.60 (m, 2 H); 1.10-0.80 (m, 3 H).

1-(1'-Nitro-1'-phenylseleno-ethyl)-pentyl-trifluoroacetate (11d). From 10.73 g (75 mmol) of 2-nitro-2-heptene and 80 mmol of $PhSeO_2CCF_3$ 29.67 g (96 %) of 11d was obtained. IR (Film): 2980 m, 1790 s, 1540 s, 1220 s, 1150 bs. ^{1}H-NMR ($CDCl_3$): δ 7.70-7.24 (m, 5 H); 5.88-5.68 (m, 1 H); 1.85 and 1.73 (s, 3 H); 1.90-1.70 (m, 2 H); 1.50-1.15 (m, 4 H); 0.95 (t, J = 5 Hz, 3 H).

2-Nitro-2-phenylseleno-heptyl-trifluoroacetate (11e). From 7.15 g (50 mmol) of 2-nitro-1-heptene and 52.5 mmol of $PhSeO_2CCF_3$ 20.2 g (98 %) of 11e was obtained as a pale yellow oil. IR (Film): 2980 m, 1795 s, 1550 s, 1340 s, 1225 s, 1170 s, 1150 s. ^{1}H-NMR ($CDCl_3$): δ 7.70-7.20 (m, 5 H); 4.88-4.60 (AB syst., J_{AB} = 9 Hz, 2 H); 2.24 (bt, J = 7 Hz, 2 H); 1.70-1.10 (bm, 6 H); 0.88 (bt, J = 4 Hz, 3 H).

1-(1-nitro-1-phenylseleno-ethyl)-hexyl-trifluoroacetate (11f). From 2.35 g (15 mmol) of (E)-2-nitro-2-octene and 15 mmol of $PhSeO_2CCF_3$ 5.95 g (93 %) of 11f was obtained as a single diastereomer. IR (Film): 2980 m, 1795 s, 1550 s, 1225 s, 1175 s, 1150 s. ^{1}H-NMR ($CDCl_3$): δ 7.70-7.25 (m, 5 H); 5.86-5.70 (dxd, J_1 = 9 Hz, J_2 = 1.5 Hz, 1 H); 0.87 (bs, 5 H); 1.55-1.20 (bs, 6 H), 0.90 (bt, J = 6 Hz, 3 H).

2-Nitro-2-phenylseleno-cyclohexyl-trifluoroacetate (11g). From 0.635 (5 mmol) of 1-nitrocyclohexene, 0.965 g (5 mmol) of benzeneselenyl chloride, 1.10 g (5 mmol) of silvertrifluoroacetate, 1.88 g (95 %) of 11g was obtained. IR (Film): 2950 m, 1790 s, 1545 s, 1225 bs, 1170 s, 1150 s. ^{1}H-NMR ($CDCl_3$): δ 7.70–7.30 (m, 5 H); 5.73 (bs, 1 H); 2.50–1.50 (m, 8 H). MS *m/e*: 396, 350, 236, 157, 46.

General procedure for the hydrolysis of the trifluoroacetate group to the nitroselenoalkanols (12).

Method A: Hydrolysis of primary trifluoroacetate. A 10 mmol run is described. 10 mmol of the corresponding trifluoroacetate was stirred in 5–10 ml methanol for 20–24 h. The solvent was removed on a rotatory evaporator and the residue was purified by crystallization or flash chromatography.

Method B: Hydrolysis of secundary trifluoroacetate. A 60 mmol run is described. To a solution of 60 mmol of the corresponding trifluoroacetate in 200 ml methanol was added a solution of 2.5 g $NaHCO_3$ in 50 ml water. Stirring was continued for 10–50 min. After adding of 50 ml water, the reaction mixture was extracted with 3x200 ml CH_2Cl_2. The organic layer was dried over $MgSO_4$ and filtered. The solvent was removed by rotatory evaporator and the residue was purified by crystallization or flash chromatography.

Note: The crude product of the hydrolysis can be directly oxidised to the hydroxynitroolefin, thus improving the overall yield, since the selenides were found to decompose partially during purification by silicagel flash chromatography.

2-Nitro-2-phenylselenopropan-1-ol (12a). Methanolysis (Method A) of the crude 11a gave after recrystallization from ether/pentane 12a in 90 % yield (from 2-nitropropene). M.p. 72–74°C; IR (KBr): 3420 bm, 1540 s, 1440 m, 1340 m, 690 m. ^{1}H-NMR ($CDCl_3$): δ 7.70–7.40 (m, 5 H); 4.20–3.85 (AB syst., J_{AB} = 12 Hz, 2 H); 1.95 (s, 1 H); 1.82 (s, 3 H). MS *m/e*: 261, 244, 243, 157, 43, 18. (Found: C, 41.57; H, 4.26; N, 5.38. Calc for $C_9H_{11}NO_3Se$: C, 41.55; H, 4.26; N, 5.38.)

3-Nitro-3-phenylseleno-butan-2-ol (12b). Hydrolysis (Method B) of the crude 11b gave after flash-chromatography (ether/petrolether 1:3) 12b in 70 % yield from 2-nitro-2-butene. IR (Film): 3500 bm, 1570 m, 1535 s, 1440 m, 740 s, 695 s. ^{1}H-NMR ($CDCl_3$): δ 7.72–7.20 (m, 5 H); 4.60–4.20 (m, 1 H); 3.10 (bs, 1 H); 1.70 and 1.56 (s, 3 H); 1.35 and 1.25 (d, J = 6 Hz, 3 H). (Found: C, 44.14; H, 5.10; N, 4.65. Calc for $C_{10}H_{13}NO_3Se$: C, 43.81; H, 4.78; N, 5.11.)

2-Nitro-2-phenylseleno-pentan-3-ol (12c). Hydrolysis (Method B) of the crude 11c gave 12c in 93 % crude yield from 2-nitro-2-pentane. The product was oxidised without further purification. IR (Film): 3500 bm, 1580 w, 1540 s, 1480 m, 750 s, 700 m. ^{1}H-NMR ($CDCl_3$): δ 7.70–7.18 (m, 5 H); 4.15–3.92 (m, 1 H); 2.92 (bs, 1 H); 1.90–1.30 (m, 2 H); 1.70 and 1.60 (s, 3 H); 1.02 (t, J = 6 Hz, 3 H).

2-Nitro-2-phenylseleno-heptan-3-ol (12d). Hydrolysis (Method B) of the crude 11d gave 12d in 95 % crude yield from 2-nitro-2-heptene. An analytical sample was obtained by flash chromatography (ether/pentane 1:6). IR (Film): 3500 bm, 2980 s, 2950 s, 1535 s, 740 s, 690 m. ^{1}H-NMR ($CDCl_3$): δ 7.70–7.32 (m, 5 H); 4.26–4.05 (m, 1 H); 2.55 (bs, 1 H); 1.70 and 1.62 (s, 3 H); 1.60–1.15 (m, 4 H); 1.06–0.80 (m, 3 H). MS *m/e*: 316, 314, 157, 69, 57, 43, 18.

2-Nitro-2-phenylseleno-heptan-1-ol (12e). Methanolysis (Method A) of crude 11e gave 12e in 98.9 % crude yield from 2-nitro-1-heptene. IR (Film): 3450 bm, 1535 s, 1440 m, 745 s, 695 m. ^{1}H-NMR ($CDCl_3$): δ 7.65–7.10 (m, 5 H); 4.00 (s, 2 H); 2.80 (s, 1 H); 2.20–1.90 (m, 2 H); 1.65–1.05 (m, 6 H); 0.82 (tb, J = 6 Hz, 3 H).

2-Nitro-2-phenylseleno-octan-3-ol (12f). Hydrolysis (Method B) of the crude 11f gave after flash chromatography (ether/petrolether 1:6) 12f in 75 % yield from 2-nitro-2-octene. IR (Film): 3480 bm, 2960 s, 2940 s, 1540 s, 745 m. ^{1}H-NMR ($CDCl_3$): δ 7.65–7.22 (m, 5 H); 4.25–4.06 (m, 1 H); 2.34 (bs, 1 H); 1.90–1.60 (m, 2 H); 1.66 (s, 3 H); 1.50–1.15 (m, 6 H); 1.05–0.80 (m, 3 H). MS *m/e*: 314, 185, 157, 55, 43, 18. (Found: C, 51.49; H, 6.65; N, 4.09. Calc for $C_{14}H_{21}NO_3Se$: C, 50.91; H, 6.41; N, 4.24.)

2-Nitro-2-phenylseleno-cyclohexanol (12g). Hydrolysis of crude 11g gave after recrystallization from ether/pentane 12g as pale yellow crystals. Yield: 80 % from 1-nitrocyclohexene. IR (KBr): 3380 bs, 2970 m, 2960 m, 1535 s, 745 s, 695 m. ^{1}H-NMR ($CDCl_3$): δ 7.60–7.20 (m, 5 H); 4.32–4.12 (m, 1 H); 3.08–2.80 (bs, 1 H); 2.30–1.20 (m, 8 H). MS *m/e*: 314, 157, 70, 57, 44, 28, 18. (Found: C, 48.23; H, 5.37; N, 4.47. Calc for $C_{12}H_{15}NO_3Se$: C, 48.01; H, 5.04; N, 4.67.)

General procedure for the oxidative elimination of the phenylseleno group to afford the nitroallylic alcohols 13.

A 10 mmol run is described. To a yellow-orange solution of 10 mmol of the nitrophenylselenoalkanol 12 in 60 ml THF was added 100 mmol 35 % H_2O_2 solution (~ 10 ml) at 0°C over a period of 15 min. After 20 min. the cooling bath was removed and the solution allowed to warm up. When the mixture reached 20–25°C, bubbling occured and the mixture warmed rapidly up (use caution in large scale reaction). The reaction flask was cooled in the ice bath until the temp. of the solution returned to *ca.* 10°C, at which point the bath was removed again and stirring was continued for 30 min. at room temp. The mixture was poured into 60 ml ether and extracted twice with 30–50 % acq. $NaHCO_3$, with H_2O and brine. After drying over $MgSO_4$ the solvent was removed in vacuo. Flash chromatography or distillation gave analytically pure products. The crude product of the oxidative elimination can be pivalated without further purification.

2-Nitro-2-propen-1-ol (13a). From 540 mg (2.07 mmol) of 12a and 2.3 ml of 35% H_2O_2 (*ca.* 20 mmol) 180 mg (84.5 %) of 12a was obtained after Kugelrohr distillation. B.p. 100–120°C/15 mm Hg. IR (Film): 3400 bm, 2980 m, 1540 s, 1350 m, 960 m. ^{1}H-NMR ($CDCl_3$): δ 6.6 (d, J = 1 Hz, 1 H);

5.93 (bs, 1 H); 4.56 (s, 2 H); 2.75 (s, 1 H).

2-Nitro-1-propen-1-ol (13b). Treatment of 890 mg (3.25 mmol) of 12b 3.2 ml of 35 % H_2O_2 (*ca.* 30 mmol) gave after flash chromatography (ether/petrolether 1:1.5) 230 mg (61 %) of 13b as a pale yellow liquid. IR (Film): 3400 bm, 2980 m, 1520 s, 1350 s, 960 m, 880 m. ^{1}H-NMR ($CDCl_3$): δ 6.55 (d, J = 3 Hz, 1 H); 5.90 (bs, 1 H); 5.02-4.80 (m, 1 H); 2.78 (bd, J = 4.5 Hz, 1 H); 1.48 (d, J = 6 Hz). MS *m/e*: 116, 102, 43, 18.

2-Nitro-1-penten-3-ol (13c). Treatment of 14.0 g (48.6 mmol) of 12c with 45 ml of 35 % H_2O_2 (*ca.* 43 mmol) in 300 ml of THF gave after flash chromatography (petrolether/CH_2Cl_2/MeOH 10:5:0.5) 3.3 g (51.8 % from 2-nitro-2-pentene) of 13c. B.p. 60-70°C/0.01 mm HG. IR (Film): 3400 bm, 2960 s, 2940 s, 1520 s, 1460 m, 1350 s. ^{1}H-NMR ($CDCl_3$): δ 6.55 (d, J = 2 Hz, 1 H); 5.30 (bs, 1 H); 4.66 (t, J = 6 Hz, 1 H); 2.96 (s, 1 H); 1.92-1.60 (m, 2 H); 1.00 (t, J = 6 Hz, 3 H). MS *m/e*: 102, 85, 57, 44, 41, 18. (Found: C, 46.25; H, 7.30; N, 10.61. Calc for $C_5H_9NO_3$: C, 45.79; H, 6.92; N, 10.68.)

2-Nitro-1-hepten-3-ol (13d). From 10 g crude 12d and 21 ml of 35 % H_2O_2 (*ca.* 30 mmol) 3.4 g (68 % from 2-nitro-2-heptene) of 13d was obtained after Kugelrohr distillation. B.p. 60-70°C/6·10^{-5} mm Hg. IR (Film): 3440 bm, 2960 s, 1700 w, 1525 s. ^{1}H-NMR ($CDCl_3$): δ 6.52 (d, J = 2.5 Hz, 1 H); 5.88 (bs, 1 H); 4.62 (t, J = 6 Hz); 3.52 (s, 1 H); 1.90-1.60 (m, 2 H); 1.58-1.20 (m, 4 H); 0.90 (t, J = 6 Hz, 3 H). MS *m/e*: 113, 102, 57, 43, 41, 18.

2-Nitro-2-hepten-1-ol (13e). From 14.1 g crude 12e and 45 ml of 35 % H_2O_2 6.42 g (60 % from 2-nitro-1-heptene) of 13e was obtained. Flash chromatography (petrolether/CH_2Cl_2/MeOH 10:5:0.5) gave an analytically pure sample. IR (Film): 3400 bm, 2960 s, 1750 m, 1660 m, 1520 s. ^{1}H-NMR ($CDCl_3$): δ 7.28 (t, J = 9 Hz); 4.55 (s, 2 H); 2.84 (brs, 1 H); 2.50-2.22 (4-line syst., 2 H); 1.70-1.15 (m, 4 H); 0.93 (t, J = 6 Hz). MS *m/e*: 142, 95, 57, 43, 41, 18. (Found: C, 53.55; H, 8.35; N, 8.38. Calc for $C_7H_{13}NO_3$: C, 52.82; H, 8.23; N, 8.80.)

2-Nitro-1-octen-3-ol (13f). Treatment of 530 mg (1.60 mmol) of 12f with 1.6 ml of 35 % H_2O_2 (*ca.* 16 mmol) gave after flash chromatography (ether/pentane 1:1.5) 200 mg (72 %) of 13f as a pale yellow liquid. IR (Film): 3430 bm, 2960 s, 2940 s, 1705 m, 1525 s. ^{1}H-NMR ($CDCl_3$): δ 6.50 (d, J = 1.5 Hz, 1 H); 5.84 (s, 1 H); 4.70 (q, J = 6 Hz, 1 H); 2.50 (d, J = 6 Hz, 1 H); 1.85-1.55 (m, 2 H); 1.55-1.20 (bs, 6 H); 0.85 (t, J = 6 Hz, 3 H). (Found: C, 55.30; H, 8.83; N, 8.21. Calc for $C_8H_{15}NO_3$: C, 55.47; H, 8.73; N, 8.09.)

2-Nitro-2-cyclohexen-1-ol (7a). Treatment of 5 mmol of 12g with 5 ml of 35 % H_2O_2 gave after flash chromatography (CCl_4/MeOH 9:1) 7a in 62 % yield.

BF_3·Etherate induced pivaloylation of nitroallylic alcohols 13.

1-(1'-Nitroethenyl)-pent-1-yl 2,2-dimethylpropanoate (14d). A mixture of 2.9 g (18.2 mmol) of 13d, 15 ml of pivalic anhydride and 0.5 ml of BF_3·OEt_2 was stirred at room temp. under argon during 7 h (^{1}H-NMR control). The excess of the anhydride was evaporated in a Kugelrohr apparatus at 60°C and 0.05 mm Hg and the residue purified by flash chromatography (Ether/pentane 1:13). Yield of pure 14d: 3.1 g (70 %) as a yellow oil. IR (Film): 2970 m, 1740 s, 1535 s, 1155 s. ^{1}H-NMR ($CDCl_3$): δ 6.56 (d, J = 1.5 Hz, 1 H); 5.94-5.73 (m, 2 H); 2.00-1.70 (m, 2 H); 1.50-1.20 (m, 4 H); 1.23 (s, 9 H); 1.03-0.80 (bt, J = 6 Hz, 3 H). MS m/e: 197, 113, 85, 57, 41. (Found: C, 59.45; H, 8.77; N, 5.59. Calc for $C_{12}H_{21}NO_4$: C, 59.24; H, 8.70; N, 5.76.)

2'-Nitro-2'-hepten-1-yl 2,2-dimethylpropanoate (14e). A mixture of 6.1 g (*ca.* 38.3 mmol) of crude 13e, 20 ml of pivalic anhydride and 1 ml of BF_3·OEt was stirred at room temp. under argon during 3 h. After evaporating of the excess anhydride, distillation of the residue (80-90°C/10^{-5} mm Hg) gave 6.85 g (73 %) of 14e as a yellow oil. An analytically pure sample was obtained by flash chromatography (petrolether/ether 11:1).

The same product was also prepared by heating a solution of 590 mg (3.7 mmol) 13d in 3.5 ml pivalic anhydride under BF_3·OEt-catalysis at 80°C during 6-8 h. Flash chromatography and distillation as above gave 615 mg (67 %) 14e. IR (Film): 2970 s, 1740 s, 1675 w, 1530 s, 1150 bs. ^{1}H-NMR ($CDCl_3$): 7.55-7.70 (t, J = 7 Hz, 1 H); 5.05 (s, 2 H); 2.52-2.22 (m, 2 H); 1.60-1.08 (m, 4 H); 1.18 (s, 9 H), 1.05-0.90 (bt, J = 6 Hz, 3 H). MS *m/e*: 244, 197, 58, 42. (Found: C, 59.44; H, 8.84; N, 5.76. Calc for $C_{12}H_{21}NO_4$: C, 59.24; H, 8.70; N, 5.76.)

General procedure for the addition of a nucleophile to substituted nitro-allylating reagents.

Method A: Direct addition (a nitroallylating reagent solution was added to the nucleophile). A 10 mmol run is described. Unless noted otherwise, 10 mmol of a ketone or ester was added to a solution of 10.5 mmol of lithiumdiisopropylamide (LDA) in 35 ml of dry THF under argon. The lithium enolate was formed after *ca.* 1 h stirring at -78°C. Then a solution of the nitroallylating reagent (10 mmol) in 50 ml THF was added within 20 min. through a teflon cannula. After 1-3 h at -78°C the mixture was poured into 120 ml of a 2 % acetic acid solution and extracted with CH_2Cl_2 (3x100 ml). The organic layer was washed successively with acq. $NaHCO_3$-solution (2x100 ml) H_2O (2x100 ml) brine, dried over $MgSO_4$ and filtered. The solvent was removed on a rotatory evaporator and the residue was purified by flash chromatography.

Method B: Inverse additon (the nucleophile is added to a nitroallylating reagent solution. Following the previously described technique[34,35], a flask A with the metal reagent was cooled to between -50°C and -80°C. A second flask B contained a stirred solution of the

nitroallylating reagent (10 mmol) in THF (50 ml) at -100°C and to this the contents of flask A were transferred through teflon cannula over a period of 15 min. After stirring for 30–120 min. (depending on the nucleophile) at -78°C, the mixture was worked up as above.

6-Nitro-5-decene (16). Method B. Butyllithium (3.5 mmol) and 830 mg (3.41 mmol) 14d gave after flash chromatography (petrolether/CH_2Cl_2 6.5:1) the product 16 (527 mg/78%) as a pale yellow liquid. IR (Film): 2960 s, 2930 s, 2840 s, 1515 s, 1335 s, 730 m. ^{1}H-NMR ($CDCl_3$): δ 7.10 (t, J = 7 Hz, 1 H); 2.60 (bt, J = 6 Hz, 2 H); 2.40–2.10 (m, 2 H); 1.70–1.20 (m, 10 H); 0.95 (m, 6 H). MS *m/e*: 200, 183, 69, 55, 43, 41. (Found: C, 66.33; H, 10.72; N, 7.10. Calc for $C_{11}H_{21}NO_2$: C, 66.29; H, 10.62; N, 7.03.)

3-Butyl-2-nitro-1-heptene (17). Method B. From 690 mg (2.8 mmol) of 14e and 2.9 mmol of *n*-BuLi 390 mg (70 %) of 17 was obtained after flash chromatography (CH_2Cl_2/petrolether 1:1). IR (Film): 2960 s, 2930 s, 1525 s, 1460 m. ^{1}H-NMR ($CDCl_3$): δ 6.45 (d, J = 1 Hz, 1 H); 5.45 (bs, 1 H); 3.05–2.75 (q, J = 6 Hz, 1 H); 1.70–1.05 (m, 12 H); 1.00–0.80 (bt, J = 6 Hz, 6 H). MS *m/e*: 200, 156, 95, 69, 57, 41. (Found: C, 66.31; H, 10.66; N, 7.07. Calc for $C_{11}H_{21}NO_2$: C, 66.29; H, 10.62; N, 7.03.)

2-(2-Nitro-2-heptenyl)-cyclopentanone (18). Method A. From 486 mg (2 mmol) of 14d and 168 mg (2 mmol) of cyclopentanone 335 mg (75 %) of 18 was obtained after flash chromatography (CH_2Cl_2/petrolether 1:1). IR (Film): 2950 s, 2920 s, 1735 s, 1510 s, 1330 s. ^{1}H-NMR ($CDCl_3$): δ 7.20 (t, J = 9 Hz, 1 H); 3.18–2.83 (m, 1 H); 2.70–1.80 (m, 8 H); 1.80–1.10 (m, 6 H); 0.90 (bt, J = 6 Hz, 3 H). MS *m/e*: 226, 279, 95, 67, 41. (Found: C, 63.88; H, 8.46; N, 6.18. Calc for $C_{12}H_{19}NO_3$: C, 63.98; H, 8.50; N, 6.21.)

2-[1-(1-Nitroethenyl)pentyl]-cyclopentanone (19). Method A. Cyclopentanone (126 mg/1.5 mmol) and 14e (360 mg/1.48 mmol) gave after flash chromatography (CH_2Cl_2/petrolether 1:1) 240 mg (71.6 %) of 19 (60 % ds). IR (Film): 2960 s, 2930 s, 1735 s, 1525 s, 1340 m. ^{1}H-NMR ($CDCl_3$): δ 6.56 and 6.50 (d, J = 2 Hz, 1 H); 5.60–5.45 (m, 1 H); 3.50–3.20 and 3.18–2.80 (m, 1 H); 2.50–1.10 (m, 13 H); 0.90 (bt, J = 6 Hz, 3 H). MS *m/e*: 226, 179, 137, 84, 41. (Found: C, 63.52; H, 8.60; N, 6.03. Calc for $C_{12}H_{19}NO_3$: C, 63.97; H, 8.50; N, 6.22.)

2-(2-Nitro-2-heptenyl)-cyclohexanone (20). Method A. From 480 mg (1.97 mmol) of 14d and 196 mg (2 mmol) of cyclohexanone, 380 mg (80 %) of 20 was obtained after flash chromatography (CH_2Cl_2/petrolether 1:1). IR (Film): 2940 s, 2980 s, 1740 s, 1520 s. ^{1}H-NMR ($CDCl_3$): δ 7.24 (t, J = 9 Hz, 1 H); 3.20–2.78 (m, 1 H); 2.60–1.05 (m, 16 H); 0.95 (bt, J = 5 Hz, 3 H).

2-[1-(1-Nitroethenyl)pentyl]-cyclohexanone (21). Method A. Cyclohexanone (490 mg/5 mmol) and 14e (1.215 g/5 mmol) gave after flash chromatography (CH_2Cl_2/petroether 1:1) 880 mg (74 %) of 21 as a 75:25 diastereomer mixture. IR (Film): 2960 s, 2940 s, 1705 s, 1650 w, 1520 s. ^{1}H-NMR ($CDCl_3$): δ 6.54 and 6.47 (d, J = 2 Hz, 1 H); 5.54 and 5.50 (d, J = 1.5 Hz, 1 H); 3.64–3.04 (m, 1 H); 2.90–1.10 (m, 15 H); 0.85 (bt, J = 4.5 Hz, 3 H). MS *m/e*: 194, 193, 98, 41, 27. (Found: C, 65.32; H, 8.79; N, 5.88. Calc for: C, 65.24; H, 8.85; N, 5.85.)

N-Methyl-3-(2-nitro-2-heptenyl)-indole (22). A mixture of 364 mg (1.5 mmol) of 14d and 197 mg (1.5 mmol) of N-methyl-indole in 7.5 ml of benzene was stirred at room temp. for 11 days. Flash chromatography (CH_2Cl_2/petrolether 1:2) of the crude product gave 307 mg (75 %) 22 as a yellow oil. IR (Film): 2960 m, 1660 w, 1615 w, 1520 s, 1330 s, 740 s. ^{1}H-NMR ($CDCl_3$): δ 7.50–7.35 (m, 1 H); 7.20–6.88 (m, 4 H); 6.70 (s, 1 H); 3.97 (s, 2 H); 3.58 (s, 3 H); 2.50–2.20 (m, 2 H); 1.60–1.20 (m, 4 H); 1.00–0.80 (m, 3 H). MS *m/e*: 272, 226, 183, 144, 95. (Found: C, 70.71; H, 7.60; N, 10.17. Calc for $C_{16}H_{20}N_2O_2$: C, 70.56; H, 7.40; N, 10.29.)

N-Methyl-3-[1-(1-nitroethenyl)pentyl]-indole (23). A mixture of 364 mg (1.5 mmol) 14e and 196 mg (1.5 mmol) N-methyl-indole in 7.5 ml benzene was stirred at room temp. for 4 days and refluxed for another 4 days. Flash chromatography of the product mixture, which contained unreacted N-methyl-indole, mono- and diadduct, gave 23 in 20 % yield. ^{1}H-NMR ($CDCl_3$): δ 7.50–7.34 (m, 1 H); 7.20–6.90 (m, 3 H); 6.80 (s, 1 H); 6.30 (d, J = 1 Hz, 1 H); 5.40 (s, 1 H); 4.40 (t, J = 7.5 Hz, 1 H); 3.63 (s, 3 H); 2.10–1.80 (m, 2 H); 1.50–1.15 (m, 4 H); 0.75 (bt, J = 6 Hz, 3 H).

6-Butyl-1-nitrocyclohexene (24). Method B. Butyllithium (10 mmol) and 2.27 g (10 mmol) of 7b gave after distillation (65°C/0.02 mm Hg) 150 g (82 %) of 24. IR (CCl_4): 2950 m, 2860 m, 1660 w, 1515 s. ^{1}H-NMR (CCl_4): δ 7.11 (t, J = 4.5 Hz, 1 H); 2.9 (m, 1 H); 2.30 (m, 2 H); 1.90–1.10 (m, 10 H); 0.9 (m, 3 H). MS *m/e*: 183, 166, 137, 79, 41. (Found: C, 66.71; H, 9.43; N, 7.64. Calc for $C_{10}H_{17}NO_2$: C, 66.54; H, 9.35; N, 7.64.

1-Nitro-6-phenylcyclohexene (25). Method B. A solution of 4.94 ml (7.6 mmol) of BuLi in hexane (1.54 M) was added dropwise to 1.185 g (7.55 mmol) of bromobenzene in 50 ml of THF at -90°C. Stirring was continued for 1 h at -90°C. This mixture was then transferred within 20 min. to a flask containing a stirred solution of 1.697 g (7.48 mmol) of 7b in 50 ml of THF at -100°C. Usual workup gave 1.34 g (89 %) 25. M.p. 58°C. IR (CCl_4): 3090 w, 2950 m, 1665 w, 1600 w, 1520 s, 1490 m. ^{1}H-NMR (CCl_4): δ 7.40 (t, J = 4 Hz, 1 H); 7.12 (m, 5 H); 4.16 (m, 1 H); 2.32 (m, 2 H); 1.84 (m, 2 H); 1.48 (m, 2 H). MS *m/e*: 168, 157, 156, 127, 41. (Found: C, 70.86; H, 6.46; N, 6.89. Calc for $C_{12}H_{13}NO_2$: C, 70.92; H, 6.45; N, 6.89.)

2-(2-Nitro-2-cyclohexenyl)-2-phenyl-1,3-dithiane (26). Method B. A solution of 7.3 mmol BuLi in hexane was added slowly to a solution of 890 mg (7.32 mmol) of 2-phenyl-1,3-dithiane in 15 ml THF at -78°C. Stirring was continued for 2 h at -78°C. This mixture was then transferred over a period of 20 min. to a flask containing a stirred solution of 1.66 g (7.3 mmol) of 7b at -100°C. Usual workup gave 1.478 g (63 %) of 26. M.p. 155°C. IR ($CDCl_3$): 2970 m, 2920 m, 1660 m, 1520 s. ^{1}H-NMR

(CCl_4/$CDCl_3$): δ 7.95 (m, 2 H); 7.34 (m, 3 H); 7.08 (t, J = 4 Hz, 1 H); 3.80 (m, 1 H); 2.20 (m, 2 H); 2.00-1.30 (m, 6 H). MS *m/e*: 322, 321, 195, 121, 41. (Found: C, 59.71; H, 5.94; N, 4.20; S, 19.90. Calc for $C_{18}H_{19}NO_2S_2$: C, 59.78; H, 5.96; N, 4.36; S, 19.95.

6-(Methylphenylamino)-1-nitro-2-cyclohexene (27). N-Methyl aniline (1.071 g/10 mmol) and 2.27 g (10 mmol) of 7b in 23 ml of THF was refluxed for 6 days. Flash chromatography gave 1.53 g (66 %) of 27 as a yellow oil. IR (CCl_4): 3100 m, 2960 m, 1670 w, 1600 w, 1528 s, 1508 m. ^{1}H-NMR (CCl_4): δ 7.15 (3-line syst., 3 H); 6.80 (m, 3 H); 5.00 (bs, 1 H); 2.72 (s, 3 H); 2.3 (m, 2 H); 2.05-1.55 (m, 4 H).

3-(2-Nitro-2-cyclohexenyl)-N-methylindole (28). An equimolar solution of N-methylindole and 7c in benzene (18 ml pro 10 mmol N-methylindole) was refluxed for 40 h. Flash chromatography gave a yellow oil that slowly crystallized. Yield 77 %. M.p. 71°C. IR (CCl_4): 2980 m, 1670 m, 1620 w, 1520 s. ^{1}H-NMR (CCl_4): δ 7.48 (m, 1 H); 7.25 (t, j = 4 Hz); 7.10-6.80 (m, 3 H); 6.46 (s, 1 H); 4.53 (m, 1 H); 3.41 (s, 3 H); 2.30 (m, 2 H); 1.88 (m, 2 H); 1.48 (m, 2 H). MS *m/e*: 257, 256, 209, 181, 146, 42. (Found: C, 70.33; H, 6.25; N, 10.81. Calc for $C_{15}H_{16}N_2O_2$: C, 70.29; H, 6.29; N, 10.93.)

1,3-Bis-(2,2-dimethylpropoxycarbonylmethyl)-2--nitroindane (29). Tert.-butylacetat (655 mg, 5.64 mmol) and 548 mg (2.85 mmol) of 8b gave after flash chromatography (CH_2Cl_2) 2.1 g (93.5 %) of 29 as a 11:26:63 diastereomer mixture. IR ($CHCl_3$): 3020 m, 2990 s, 1725 s, 1550 s. ^{1}H-NMR ($CDCl_3$): δ 7.35-7.10 (m, 4 H); 5.69 (t, J = 6 Hz); 5.42 (dxd, J_1 = 4.1 Hz, J_2 = 7.7 Hz); 5.09 (t, J = 7.3 Hz); 4.19 (dxdxd, J_1 = J_2 = J_3 = 7 Hz); 3.99 (dxdxd, J_1 = 8.5 Hz, J_2 = J_3 = 6 Hz); 3.02-2.44 (m, 4 H); 1.50, 1.48, 1.44, 1.42 (s, 18 H). MS *m/e*: 318, 262, 233, 57, 41. (Found: C, 64.58; H, 7.45; N, 3.67. Calc for $C_{21}H_{29}NO_6$: C, 64.43; H, 7.47; N, 3.58.)

4-Nitro-3-phenyl-4-pentenoic acid-methylester (30). Methylacetate (755 mg/10.2 mmol) and 2.63 g (10 mmol) of 9 gave after flash chromatography (CH_2Cl_2/pentane 2:3) 1.1 g (47 %) of 30. IR (Film): 2960 m, 1735 s, 1525 s, 700 s. ^{1}H-NMR ($CDCl_3$): δ 7.25 (s, 5 H); 6.60 (d, J = 2 Hz, 1 H); 5.65 (bs, 1 H); 4.80 (t, J = 7.5 Hz); 3.60 (s, 3 H), 2.88 (d, J = 7.5 Hz, 2 H). MS *m/e*: 204, 188, 160, 115, 59, 41.

2-(2-Nitro-1-phenyl-2-propenyl)-cyclohexanone (31). From 2.63 g (10 mmol) of 9 and 1 g (10.2 mmol) of cyclohexanone 1.5 g (58 %) 31 was obtained as a diastereomer mixture (75 % ds). Flash chromatography gave 960 mg (37 %) of the major diastereomer with > 95 % ds and 280 mg (10 %) of the minor diastereomer. Major: M. p. 101-102°C. IR ($CHCl_3$): 2950 m, 2870 m, 1715 s, 1530 s, 1450 m. ^{1}H-NMR ($CDCl_3$): δ 7.23 (bs, 5 H); 6.44 (d, J = 3 Hz, 1 H); 5.53 (d, J = 3 Hz, 1 H); 4.48 (d, J = 10 Hz, 1 H); 2.95 (dxt), J_1 = 7 Hz, J_2 = 10 Hz, 1 H); 2.38 (d, J = 7 Hz, 2 H); 1.7 (m, 6 H). MS *m/e*: 213, 183, 128, 115, 41. (Found: C, 69.12; H, 6.52; N, 5.66. Calc for $C_{15}H_{17}NO_3$: C, 69.48; H, 6.61; N, 5.40.) Minor: IR ($CHCl_3$): 2950 m, 2870 m, 1715 s, 1525 s. ^{1}H-NMR ($CDCl_3$): δ 7.26 (s, 5 H); 6.52 (s, 1 H); 5.68 (s, 1 H); 4.60 (d, J = 10 Hz, 1 H); 3.45 (m, 1 H); 2.38 (m, 2 H); 1.80 (m, 6 H).

2-Nitro-3-phenyl-heptene (32). From 2.63 g (10 mmol) of 9 and 10.5 mmol of *n*-BuLi 2.03 g (93 %) of 32 was obtained after Kugelrohr distillation. B.p. 70°C/10^{-5} mm Hg; IR (CCl_4): 3090 s, 1600 m, 1520 s, 1340 m. ^{1}H-NMR (CCl_4): δ 7.2 (bs, 5 H); 6.4 (m, 1 H); 5.49 (s, 1 H); 4.08 (t, J = 7 Hz, 1 H); 2.0-1.6 (m, 2 H); 1.5-1.0 (m, 4 H); 0.85 (t, J = 6 Hz, 3 H). MS *m/e*: 220, 219, 130, 91, 41. (Found: C, 70.59; H, 7.36; N, 6.43. Calc for $C_{13}H_{17}NO_2$: C, 71.21; H, 7.81; N, 6.39.

1-(2-Oxo-cyclohexyl)-3-phenyl-heptan-2-one (33) To a solution of 730 mg (3.33 mmol) 32 in 2.5 ml CH_2Cl_2 was added at -78°C 867 mg (3.33 mmol) $SnCl_4$ in 6 ml CH_2Cl_2. Trimethylsilyloxy cyclohexene (567 mg, 3.33 mmol) was added within 5 min. After completion of the addition the resulting solution was stirred at -78°C for an additional hour, then the bath temp. was gradually warmed to room temp. over a period of 3-3.5 h. The reaction was quenched with 5 ml H_2O and the resulting mixture was stirred at reflux for 2 h. The reaction mixture was extracted with CH_2Cl_2 and the combined organic layer was washed with H_2O and brine, dried over $MgSO_4$ and filtered. After removal of the solvent the residue was purified by flash chromatography and distilled (b.p. 150°C/10^{-5} mm Hg). Yield of pure 33 (3:1 diastereomer mixture): 45 %. Major diastereomer: ^{1}H-NMR (CCl_4): δ 7.20 (m, 5 H); 3.68 (t, J = 7 Hz, 1 H); 2.9-2.6 (m, 2 H); 2.5-1.0 (m, 15 H); 0.89 (t, J = 6 Hz, 3 H). Minor diastereomer: IR (CCl_4): 2965 m, 1712 s, 1602 m, 1498 m. ^{1}H-NMR (CCl_4): δ 7.20 (m, 5 H); 3.50 (t, J = 7 Hz); 2.90-2.40 (m, 2 H); 2.30-1.00 (m, 15 H); 0.89 (t, J = 6 Hz, 3 H). MS *m/e*: 211, 139, 121, 55, 41, 29. (Found: C, 79.85; H, 9.19. Calc for $C_{19}H_{26}O_2$: C, 79.68; H, 9.15.

3,4-Dimethyl-1-nitro-1-(1-phenylpentyl)-3-cyclohexene (34). A mixture of 500 mg (2.28 mmol) of nitroolefine 32, 4 ml of 2,3-dimethylbutadiene and 5 mg of hydroquinone was heated at 60°C for 40 h. The excess of diene was removed by evaporation. Flash chromatography and Kugelrohr distillation (b.p. 170°C/0.05 mm Hg) gave 611 mg (89 %) of 34 as a 3:2 diastereomer mixture. IR (CCl_4): 2978 m, 2950 m, 1608 m, 1540 s, 1500 m. ^{1}H-NMR (CCl_4): δ 7.20 (m, 5 H); 3.10 (m, 1 H); 2.90-0.95 (m, 12 H); 0.83 (t, J = 6 Hz, 3 H). MS *m/e*: 255, 254, 197, 91, 77, 41. (Found: C, 75.58; H, 8.83; N, 4.66. Calc for $C_{19}H_{27}NO_2$: C, 75.71; H, 9.03; N, 4.65.)

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